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| (51) International Patent Classification ⁵ : C08G 65/32, D01C 3/00 C11B 11/00, C08F 20/56 | A1 | (11) International Publication Number: WO 94/00508 (43) International Publication Date: 6 January 1994 (06.01.94) |
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| (54) Title: SURFACTANTS DERIVED FROM POLYOXYALKYLENES AND SUBSTITUTED SUCCINIC ANHY- DRIDES (57) Abstract Polyoxylalkylene esters and amides of alk(en)yl succinic anhydrides, of the formulae (I) $YA^1.OC(HR)CC(HR^1)CO.A(C_mH_{2m}O)_n.R^2$ and (II) $YA^1.OC(HR)CC(HR^1)CO.A(C_mH_{2m}O)_n.C_pH_{2p}.A.CO(HR^1)CC(HR)CO.A^1Y$ where R, R ¹ , A, A ¹ , Y, R ² , m, n and p are as defined, particularly where the alk(en)yl group is a C ₁₄ to C ₂₂ group, are effective surfactants. They are especially notable because, very surprisingly, the cloud point tends to rise with increasing alk(en)yl group chain length. The surfactants are ef- fective in scouring wool and inverting polyacrylamide water in oil emulsions into water. | | |

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SURFACTANTS DERIVED FROM POLYOXYALKYLENES AND SUBSTITUTED SUCCINIC ANHYDRIDES.

This invention relates to surfactants and in particular to novel surfactants based on derivatives of substituted succinic acids and to particular end uses for these surfactants.

5 In recent years there has been an increasing desire to replace well established surfactants with materials of increased biodegradability. There is, however, great practical difficulty in devising alternatives to substances of excellent performance which have maintained an important position in the market for several decades.

10 EP 0107199 B relates to polyoxyalkylene glycol hemi-esters of C₈ to C₁₂ alk(en)yl substituted succinic acids and their salts. These materials are described as anionic surfactants with particular utility at acidic pHs and having hard water tolerance.

15 This invention is based on the discovery of compounds which can be derived from alkenyl succinic anhydrides having particularly C₁₄ to C₂₂ alk(en)yl groups and/or substituents of functional groups elsewhere around the molecule give materials which have significantly and surprisingly different properties. In particular they perform well as non-ionic surfactants, particularly in aqueous systems, having
20 unexpected cloud point properties indicating good performance at elevated temperatures and have good behaviour in alkaline conditions. Also the surfactants of this invention have good biodegradation properties.

25 The present invention accordingly provides a compound of the formulae (I) or (II):



where

30 one of R and R¹ is C₆ to C₂₂ alkenyl or alkyl and the other is hydrogen;

A is - O - or - NR⁴ -; where R⁴ is hydrogen or C₁ to C₆ alkyl, particularly methyl or ethyl;

n is 2 to 100 (and as it is an average it may be non-integral);

35 m is 2 or 3 (and may vary along the poly oxyalkylene chain);

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R^2 is hydrogen or C_1 to C_6 alkyl;

A^1 is - O -, - O⁻ or -NR⁴-

where R^4 is hydrogen or C_1 to C_6 alkyl, particularly methyl or ethyl;

such that

when A^1 is - O⁻:

Y is a cation, particularly H⁺, and alkali metal cation especially a sodium or potassium cation, or an ammonium ion (especially NH₄⁺, an amine ammonium or an alkanolamine ammonium ion); and

when A^1 is - O - or -NR⁴-:

Y is a C_1 to C_6 alkyl group (R^3) or a group of the formula $(C_mH_{2m}O)_n.R^2$ where m, n and R^2 are independently as defined above;

provided that when A is - O - or A^1 is - O⁻ the total number of carbon atoms in the groups R, R^1 and any groups R^2 and R^3 is at least 13, and is desirably 13 to 50;

or

$Y.A^1.OC.(HR)C.C(HR^1).CO.A.(C_mH_{2m}O)_n.C_pH_{2p}.A.CO.(HR^1)C.C(HR)CO.A^1.Y$

where:

(II)

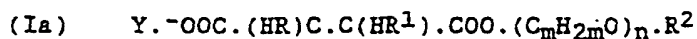
n, m and each R, R^1 , A, A^1 and Y are independently as defined above; and

p is 2 or 3.

For convenience of definition, the free acid forms of compounds of the formulae (I) and (II) in are defined with Y as a H⁺ cation. Of course, this includes both the ionised form of the free acid that will typically predominate at relatively alkaline pHs and the non-ionised form, that will typically predominate at relatively acidic pHs.

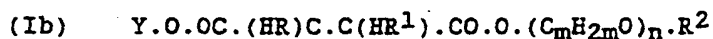
In the general formula (I), A and A^1 are desirably both - O -, both - NR⁴ -, particularly - NH -, or A is - NR⁴ -, particularly - NH -, and A^1 is - O -. Accordingly, the following particular sub-groups of compounds of the formula (I) form specific aspects of the invention (see also below about R and R^1).

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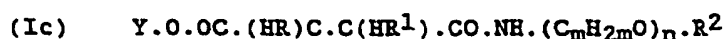
where

m, n and R^2 are as defined above for formula (I); Y is a cation as defined above for formula (I); and one of R and R^1 is a C_{14} to C_{22} , especially a C_{14} to C_{20} , alkenyl or alkyl group and the other is hydrogen.



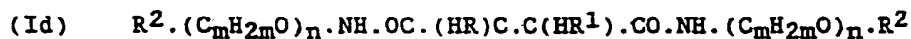
where

m, n and R^2 are as defined above formula (I); Y is a C_1 to C_6 alkyl group or a group of the formula $(C_mH_{2m}O)_n.R^2$ as defined above for formula (I); and R and R^1 are as defined above for formula (I), but particularly where one of R and R^1 is a C_{14} to C_{22} , especially a C_{14} to C_{20} , alkenyl or alkyl group and the other is hydrogen.



where

Y, m, n and R^2 are as defined above formula (I); and R and R^1 are as defined above for formula (I), but particularly where one of R and R^1 is a C_{14} to C_{22} , especially a C_{14} to C_{20} , alkenyl or alkyl group and the other is hydrogen.



where

each m, n and R^2 is independently as defined above for formula (I); and R and R^1 are as defined above for formula (I), but particularly where one of R and R^1 is a C_{14} to C_{22} , especially a C_{14} to C_{20} , alkenyl or alkyl group and the other is hydrogen.

The compounds of the general formula (II) can be considered as di(substituted succinyl) functional derivatives of a polyoxyalkylene moiety. Usually, the respective groups A and A^1 and Y will be the same. Desirably both groups A are - O - or - NR^4 -, particularly - NH -, and both groups A^1 are - O- with Y being a cation. Similarly the alk(en)yl groups in the groups R and R^1 will usually be the same.

Where, in formulae (I) and (II) Y is a cation, it is desirably H^+ , an alkali metal cation or an ammonium cation, particularly NH_4^+ , an amine ammonium cation, such as tetramethylammonium or an alkanolamine ammonium ion e.g. $HO.CH_2CH_2.NH_3^+$; where Y is a C_1 to C_6 alkyl group, it is particularly a methyl, ethyl or (straight or branched) butyl group.

The group R^2 in formulae (I) and (II) is desirably either H or a methyl, ethyl, propyl or butyl (including branched propyl and butyl) group. Where R^2 is H, the products tend to be relatively more hydrophilic and where it is an alkyl group, relatively less hydrophilic. The choice of the group R^2 will be determined by the desired overall properties of the compound.

The compounds of the invention include at least one polyoxyalkylene chain made up of residues of ethylene glycol and/or propylene glycol. The chain may be a homopolymer chain of either ethylene glycol residues or of propylene glycol residues or a block or random copolymer chain containing both ethylene glycol and propylene glycol residues. In compounds including more than one polyoxyalkylene chain, the chains can be the same or different.

Referring specifically to the polyoxyalkylene chain defined as the group $(C_mH_{2m}O)_n$ in formula (I) (including Ia, Ib and Ic) and (II). The chain length of this group, i.e. the value of the parameter n, will generally be chosen to provide the desired properties in the intended product. Typically, where the polyoxyalkylene chain is a polyethylene glycol chain it will usually have 3 to 50, particularly 3 to 35 e.g. 10 to 35, ethylene glycol residues and where it is a polyoxypropylene chain it will usually have 10 to 50 and more preferably 12 to 20 propylene glycol residues. Where the chain is a block or random copolymer of ethylene and propylene glycol residues the chain length chosen will typically correspond to the above ranges but numerically according to the proportion of ethylene and propylene glycol residues in the chain. Of course, numerical values of the repeat length of the polyoxyalkylene chain are average values. As is common to surfactants containing a polyoxyalkylene chain, the longer the chain and the higher the proportion of ethylene glycol residues, the more hydrophilic the product. In compounds of the formula (II),

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if along the polyoxyalkylene chain m is constant then p will usually be the same as m .

Among the compounds of the invention, those where the group R or R^1 is a C_{14} to C_{22} , particularly a C_{14} to C_{20} and very particularly a C_{14} to C_{18} , alkenyl or alkyl group are especially desirable.

Similarly, compounds where the group R or R^1 is an alkenyl group are more desirable than those where the group is alkyl. Compounds where the group R or R^1 is an alkenyl group, particularly a C_{14} to C_{20} alkenyl group form a specific aspect of the invention.

The compounds of this invention, and particularly those where the group R or R^1 is a C_{14} to C_{22} alkenyl or alkyl group have properties that are entirely unexpected in that the cloud point tends to rise with increasing length of the chain R or R^1 , particularly where this chain is an alkenyl chain. The step from C_{12} to C_{14} chains is often particularly notable. At chain lengths longer than C_{14} , the cloud point may tend to fall back somewhat, but often stays significantly above that for compounds with a chain length of say C_{12} . This trend in cloud point indicates increasing water solubility of the compounds with increasing chain length which is completely unexpected and runs counter to previous experience with surfactants. However, at longer chain lengths the compounds tend to be less effective wetters, which is consistent with the increasingly hydrophobic nature of the group R/R^1 . By way of example in the series of compounds of the formula: $H^+ \cdot OOC \cdot (HR)C \cdot C(HR^1) \cdot CO \cdot O \cdot (C_2H_4O)_n \cdot R^2$ where n and R^2 as given below; the cloud points ($^{\circ}C$) for compounds with R or R^1 groups in the range 10 to 18 are as follows:

| | | | | | |
|--------------------------|----|----|-------|-------|-------|
| C atoms in group R/R^1 | 8 | 12 | 14 | 16 | 18 |
| $R^2 = CH_3, n = 7$ | - | 37 | 70-81 | 52-53 | 51-52 |
| $R^2 = H, n = 8$ | <5 | 43 | 56.5 | - | - |

(The compounds in this table where $R^2 = H$ and R/R^1 chain length is 12 or less are not compounds of this invention.)

We have been unable to account for this behaviour and so far as we know it is unique in surfactants. It is of considerable practical importance in that in aqueous systems surfactants are usually most effective at or near their cloud points. Higher cloud points indicate

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materials that are likely to be effective at comparably higher temperatures and surfactants are often used at moderately superambient temperatures. The longer chain lengths are linked with increased oil solubility so the cloud point behaviour indicates that better oil solubility is likely to be linked to higher effective temperatures. This is a very useful combination of properties. This effect is more noticeable for compounds where the group R or R¹ is an alkenyl group, particularly as compounds where it is alkyl generally have lower cloud points than the corresponding alkenyl compounds.

The compounds of formula (I) where A¹ is -O⁻ and Y is H⁺ can be made by reacting an alkenyl or alkyl succinic anhydride with a compound of the formula:

H.A.(C_mH_{2m}O)_n.R² (where A, m, n and R² are as defined above).

The reaction between the anhydride and the polyalkylene glycol, polyalkylene glycol mono alkyl ether or corresponding amine derivatives can be readily carried out, with or without catalysts, by bringing the glycol or amine derivative into contact with the alkenyl or alkyl succinic anhydride. Reaction occurs typically at temperatures below 200°C and even below 100°C. The reactants will usually be used in at least approximately stoichiometric proportions. Particularly where stoichiometric proportions are used, further purification does not usually appear to be necessary, but can be carried out if desired.

The product is typically a mixture of isomers corresponding to the two senses of the anhydride ring opening reaction. We have noted that the alkenyl or alkyl chain seems to have a minor steric effect on the isomer ratio with the isomer ration being typically about 60:40, the major isomer arising from nucleophilic attack at the anhydride carbonyl group remote from the alkenyl or alkyl group.

Compounds of the invention where Y is a different cation can be made by salt formation from the free acid (Y = H⁺). Where Y is an alkali metal or ammonium cation formation of the salts is straightforward by reaction with the corresponding base e.g. alkali metal such as sodium or potassium, hydroxide or carbonate, ammonia or amine, including alkanolamines such as ethanolamine.

Compounds of the invention where A¹ is other than -O⁻ i.e. Y is other than a cation, can be made by reaction from the free acid. Typically, further reaction is by preparation of an ester,

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particularly an ester with a C₁ to C₆ or polyalkylene glycol alkyl ether alcohol. Generally longer chain esters and the corresponding amides can be made from esters with short chain alcohols, especially methyl or ethyl esters, by trans-esterification or amidation with the corresponding alcohol (YOH) or amine (YNH₂) (where Y is as defined above). The esterification of the free acid can be carried out in a conventional manner for example using an acid catalyst which may be sulphuric, toluene sulphonic or a phosphoric acid. Phosphoric acids can be particularly useful as, after neutralisation, they may be a useful component of detergent compositions which include the surfactants of this invention.

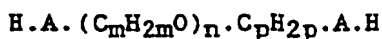
Compounds of the formulae Ia, Ib, Ic and Id can, thus, be made as follows:

- 15 Ia reacting a polyoxyalkylene glycol or derivative of the formula:
 $\text{HO} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$ with a C₁₄ to C₂₂ alk(en)yl succinic anhydride to
 give a compound of the formula:
 $\text{HOOC} \cdot (\text{HR})\text{C} \cdot \text{C}(\text{HR}^1) \cdot \text{CO} \cdot \text{O} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$
 and (where Y is other than H) reaction with an alkali material.
- 20 Ib esterifying a compound of the formula Ia, especially where Y is H, with a low molecular weight alcohol, particularly methanol, ethanol or a butanol, followed, if necessary, by a trans-esterification with an alcohol YOH to give the desired product.
- 25 Ic reacting a amino polyoxyalkylene glycol or derivative of the formula: $\text{H}_2\text{N} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$ with an alk(en)yl succinic anhydride to give a compound of the formula:
 $\text{HOOC} \cdot (\text{HR})\text{C} \cdot \text{C}(\text{HR}^1) \cdot \text{CO} \cdot \text{NH} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$
 and (where Y is other than H) reaction with an alkali material.
- 30 Id reacting a amino polyoxyalkylene glycol or derivative of the formula: $\text{H}_2\text{N} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$ with an alk(en)yl succinic anhydride to give a compound of the formula:
 $\text{HOOC} \cdot (\text{HR})\text{C} \cdot \text{C}(\text{HR}^1) \cdot \text{CO} \cdot \text{NH} \cdot (\text{C}_m\text{H}_{2m}\text{O})_n \cdot \text{R}^2$
 followed by esterification with a low molecular weight alcohol,
- 35

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particularly methanol or ethanol, followed by an amidation reaction with an amine YNH_2 to give the desired product.

Compounds of the formula (II) where Y is H^+ can be made by reacting 2 moles of an alk(en)yl succinic anhydride with one mole of a compound of the formula:



where

m, n, p and each A are independently as defined above.

Compounds where Y is another cation or a C_1 to C_6 alkyl group (R^3) or a group of the formula $(\text{C}_m\text{H}_{2m}\text{O})_n.\text{R}^2$ where m, n and R^2 are independently as defined above; can be made as described above for compounds of the formula (I).

The compounds of the invention may be made by other methods. For example, the anhydride may be reacted with a lower alcohol and the resulting half ester esterified with a polyalkylene glycol or polyalkylene glycol alkyl ether or condensed with an alkylene oxide and if desired end capped with a further lower alcohol. The polyalkylene glycol chain length can be controlled by using a polyalkylene glycol or polyalkylene glycol alkyl ether of a narrow range of molecular weight, whereas the latter process gives a wide distribution of chain lengths.

Alkenyl succinic anhydrides may be produced by reacting maleic anhydride preferably with an excess of an olefin having 6 to 22, particularly 14 to 22, carbon atoms for example a 50 to 200% excess at a temperature in the range 150 to 400°C and preferably 180 to 250°C and removing excess olefin for example by distillation which is suitably carried out under vacuum. No catalyst is necessary, but it is preferred that an antioxidant be present. These anhydrides are well known commercial materials. In alkenyl succinic anhydrides prepared as described above the double bond normally lies in the 2-position in the alkenyl substituent.

To make products where the group R or R^1 is an alkyl group then either the unsaturated products can be hydrogenated or, and preferably, the intermediate alkenyl succinic anhydride can be hydrogenated to give an alkyl succinic anhydride. Typically, the hydrogenation is carried out over a hydrogenation catalyst such as

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Raney nickel or a Pd/C catalyst. Temperatures of from 15 to 100°C and pressures of 0 - 200 bar absolute may be used and, if desired a solvent may be present. For example, the hydrogenation reaction on an alkenyl succinic anhydride may be carried out at 20°C using 5% w/w of Pd/C catalyst over a period of for example 6 to 24 hours.

It is desirable that the R, R¹ alkyl or alkenyl group of the compounds of the invention has a straight chain. Where the chain is not straight it is desirable that it has at most a total of two and preferably only one branch(es) on average. Preferably the whole molecule comprises at most three branches in total in all alkyl and alkenyl groups present.

The products are readily made with low odour and, since polyalkylene glycols and polyalkylene glycol alkyl ether or their amine derivatives are readily transportable can be made at locations distant from alkylene oxide plants if they are used as reactants.

Compounds according to the invention have emulsification properties and wetting and dispersion capabilities. These include use in oil in water emulsions for metal working fluids, based on semi-soluble oil and synthetics and for crude oil transportation and fuel systems, emollients for personal (skin) care; domestic detergent composition for example laundry liquids; the dispersion of organic and inorganic powders in paints and coatings (e.g. filler and pigments) and agrochemical formulations (e.g. pesticides); wetters in so-called industrial and institutional cleaning products (e.g. traffic film removers, bottle washes).

Particular end uses for the surfactants of this invention include wool scouring and as inverting agents in the manufacture of acrylamide or similar products. These applications are described in more detail below.

As sheared from the sheep, the woollen fleece includes, in addition to the wool fibre, a variety of materials including wool wax. Wool wax is a complex mixture of fatty materials secreted onto the wool by the skin of the sheep. Wool wax is removed from the wool, prior to use of the wool in textiles, by washing the wool with an aqueous mix including surfactants typically at moderately elevated temperatures e.g. 40 to 80°C, particularly 50 to 70°C. This process is called wool scouring. Our testing indicates that the surfactants

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of this invention are very effective wool scouring surfactants, in particular retaining their activity well after multiple scouring cycles, even when used in scouring wool with very fine fibres e.g. merino wool, which is difficult to scour because the proportion of wool fat is relatively high and the fibres have a high surface area to be treated. Although the particular choice of a compound within the invention for this end use will depend on the specific operating conditions, we have found that compounds of the formula (Ia) above, particularly where m is 2, n is from 2 to 25, particularly 3 to 10, and where R² is a C₁ to C₆ alkyl group, especially a methyl group are especially effective. The surfactant in this application is typically used at a concentration of from 0.1 to 5, particularly from 0.2 to 1.5, g.l⁻¹.

The invention accordingly includes a method of treating wool to remove wool wax which method comprises washing the wool, containing wool wax, with an aqueous mix including an effective amount of a compound of the formulae (I) or (II) above, in particular a compound of the formula (Ia) above, especially where m is 2, n is from 3 to 10 and where R² is a C₁ to C₆ alkyl group, particularly a methyl group. The invention also includes the use of such compounds of the invention as wool scouring surfactants.

The manufacture of polymers such as polyacrylamide is usually carried out by an emulsion polymerisation route in which the polymer is accumulated in an aqueous phase (in which it is soluble). It is well known that polyacrylamides can give aqueous solutions having high viscosities even at low concentrations; this is the basis of their use as thickeners and viscosity enhancers in aqueous systems. If the aqueous phase during polymerisation were the continuous phase, it would rapidly become very viscous, leading to difficulties in agitation and recovery of the product. To avoid this problem, the aqueous phase is normally the dispersed phase in an oil continuous phase i.e. as a water in oil emulsion, including an emulsifier to stabilise the water in oil emulsion. The viscosity of the oily phase does not increase during polymerisation, as does the aqueous phase, because the polymer remains in the aqueous phase. However, the polymer is typically used in a aqueous environments, so at some point the emulsion must be inverted to give an aqueous continuous phase.

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This is typically done on dilution of the water in oil emulsion into water. Usually, a surface active agent that promotes such inversion is added to the water in oil emulsion before dilution into water. Our testing indicates that the compounds of this invention are effective inverting agents for such emulsions. Although the particular choice of a compound within the invention for this end use will depend on the specific operating conditions, we have found that compounds of the formula (Ia) above, particularly where m is 2, n is from 8 to 25, particularly 10 to 15, and where R² is H or a C₁ to C₆ alkyl group, particularly a methyl, ethyl, propyl or butyl group, are especially effective. The amount of surface active agent used to invert such emulsions will depend on the emulsion, in particular the proportion of disperse aqueous phase and the polymer concentration in the aqueous phase. Generally amounts in the range 1 to 5% of the water in oil emulsion are typical.

The invention accordingly includes a method of inverting a water in oil emulsion containing polyacrylamide in the aqueous phase which comprises including in the water in oil emulsion a compound of the formulae (I) or (II) above, in particular a compound of the formula (Ia) above, especially m is 2, n is from 8 to 25, particularly 10 to 15, and where R² is H or a C₁ to C₆ alkyl group, particularly a methyl, ethyl, propyl or butyl group, and subsequently diluting the water in oil emulsion into water. The invention also includes the use of compounds of the invention as polyacrylamide water in oil emulsion inverting agents.

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The following Examples illustrate the invention including the manufacture and properties of the compounds of the invention and their end uses, particularly illustrating the versatility and utility of the compounds of the invention. All parts and percentages are by weight unless otherwise specified.

Test Methods

Cloud Point (CP)

was measured by ASTM D 2024 - 65; results are in °C

Wetting (Wtg)

Draves wetting was assessed using the skein test (ASTM D 2281 - 68); results are in seconds (s) [or minutes (m) - for slow wetters].

Foam height (FH)

Ross Miles foam height was assessed by ASTM D 1173-53 at 60°C; results are in mm.

Surface Tension (ST)

was measured on a 0.1% w/w solution by the drop method at 23°C; results are in mN.m⁻¹ (1 mN.m⁻¹ = 1 dyne.cm⁻¹).

Synthesis Examples SE1 to SE24

Various compounds of the invention were made by reacting stoichiometric mixtures of an alkenyl succinic anhydride and poly-ethylene glycol (PEG), an alkyl polyethylene glycol ether or amine derivative, as set out in Table 1 below, by heating the mixture to about 100°C. Samples taken every 30 minutes until the reaction was complete as determined by infra red spectroscopy and/or the acid value of the mixture.

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Corresponding sodium salts were made by addition of NaOH solution to the acid product until the pH had risen to 9. The sodium salt was then isolated by stripping or used as a solution in water.

5 Corresponding methyl esters were made by the addition of sulphuric acid and methanol. Methanol was distilled through the reaction at such a rate as to keep the volume constant for 2-12 hours. Sodium hydrogen carbonate was then added to neutralise the sulphuric acid and the product filtered. Other low alcohol esters were made by corresponding methods.

10 Comparative materials of similar structure were also prepared by the general method described but substituting the appropriate starting materials. These are identified by the prefix 'C' before a number.

Various properties of the compounds were measured and the results are given in Table 2 below. For further illustration a commercially
15 available nonyl phenol ethoxylate (with 9 moles of EO per mole phenol) is included in Table 2 under the reference 'NPE'.

The properties of compound SE1 are as follows:

| | | |
|----|--|----------------|
| 20 | Surface Tension (0.1% w/w solution) | |
| | (Drop Method at 23°C) mN.m ⁻¹ | 28.4 |
| | Pour Point (°C) | -15 |
| | Viscosity (cps/25°C) | 165 |
| | Foam Heights (mm) | 0 min 5 min |
| 25 | (Ross Miles at 60°C) | 7.5 3 |
| | Density (g.cm ⁻³ at 23°C) | 1.006 |
| | Wetting (Draves - seconds) | 10.5 secs |
| | Cloud Point °C | 40 - 53 |

TABLE 1

| | Ex No | Formula | R/R ¹ (1) | A | A ¹ | m | n (2) | R ² (1) | Y (1) |
|----|----------|---------|-------------------------|------|----------------|---|----------|-----------------------|----------|
| 5 | SE1 | I | 14u | -0- | -0- | 2 | 3.7 | 1 | H |
| | SE2 | I | 12u | -0- | -0- | 2 | 13.6 | H | 1 |
| | SE3 | II | 18u | -NH- | -0- | 2 | 34 | - | H |
| | SE4 | II | 12u | -0- | -0- | 2 | 18.2 | - | H |
| | SE5 | I | 12u | -0- | -0- | 2 | 7 | 1 | H |
| 10 | SE6 | I | 14u | -0- | -0- | 2 | 7 | 1 | H |
| | SE7 | I | 16u | -0- | -0- | 2 | 7 | 1 | H |
| | SE8 | I | 18u | -0- | -0- | 2 | 7 | 1 | H |
| | C1 | I | 8u | -0- | -0- | 2 | 8 | H | H |
| | C2 | I | 12u | -0- | -0- | 2 | 8 | H | H |
| | C3 | I | 12u | -0- | -0- | 2 | 12 | H | H |
| | SE9 | I | 14u | -0- | -0- | 2 | 8 | H | H |
| | SE10 | I | 12u | -0- | -0- | 2 | 4 | 1 | H |
| 15 | SE11 | I | 12u | -0- | -0- | 2 | 12 | H | 4 |
| | SE12 | I | 14u | -0- | -0- | 2 | 45 | 1 | H |
| | SE13 | I | 14u | -0- | -0- | 2 | 10 | 4 | H |
| | SE14 | I | 14u | -0- | -0- | 2 | 12 | H | 1 |
| | SE15 | I | 14u | -0- | -0- | 2 | 12 | H | 4 |
| | SE16 | I | 16u | -0- | -0- | 2 | 45 | 1 | H |
| | SE17 | I | 18u | -0- | -0- | 2 | 17 | 1 | H |
| 20 | SE18 | I | 18u | -0- | -0- | 2 | 45 | 1 | H |
| | SE19 | I | 14u | -0- | -0- | 2 | 12 | H | H |
| | SE20 | II | 12u | -0- | -0- | 2 | 34 | - | H |
| | SE21 | II | 14u | -0- | -0- | 2 | 34 | - | H |
| | SE22 | II | 14u | -NH- | -0- | 2 | 34 | - | H |
| | SE23 | II | 18u | -0- | -0- | 2 | 34 | - | H |
| | SE24 | I | 14s | -0- | -0- | 2 | 8 | H | H |
| | SE25 | I | 14s | -0- | -0- | 2 | 12 | H | H |
| 25 | SE26 | I | 18s | -0- | -0- | 2 | 12 | H | H |

- 1 the number of carbon atoms in the substituent chain is given,
for R/R¹ 'u' indicates that the substituent is an alkenyl group
's' indicates that the substituent is an alkyl group;
for R² H = hydrogen and a number the length of an alkyl group.
for Y H indicates Y = H⁺ and a number the alkyl chain length.

- 2 integral values for n may be rounded values;
for compounds of the formula (II) the value for 'n' in this table
is n+p in formula (II) as given above (with p = m).

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TABLE 2

| Ex No | ST (mN.m ⁻¹) | CP (°C) | FH (mm) | | Wtg (s) |
|----------|-----------------------------|------------|------------|------|------------|
| | | | Omin | Smin | |
| SE1 | 28.4 | 40-53 | 7.5 | 3 | 10.5 |
| SE2 | 30.3 | | 98 | 87 | |
| SE3 | 34.0 | | | | |
| SE4 | 31.9 | 10 | | | 55 |
| SE5 | 30.2 | 37 | | | 21 |
| SE6 | 30.7 | 70-81 | | | 46 |
| SE7 | - | 52-53 | | | 70 |
| SE8 | - | 51-52 | | | >300 |
| C1 | 34 | <5 | | | |
| C2 | 33.8 | 43 | | | |
| C2 | 34.6 | 54 | | | 66 |
| SE9 | 35.7 | 56.5 | | | |
| SE10 | 28.3 | 21 | | | 6.5 |
| SE11 | 31.2 | 78 | 72 | 58 | |
| SE12 | | | | | |
| SE13 | 28.8 | 60-65 | | | 14 |
| SE14 | | | | | |
| SE15 | | | | | |
| SE16 | | >96 | | | |
| SE17 | | 86-87 | | | |
| SE18 | | >96 | | | |
| SE19 | 38.7 | 66 | | | |
| SE20 | 31.6 | 63 | | | |
| SE21 | 35.1 | | | | |
| SE22 | 34.1 | | | | |
| SE23 | 34.0 | | | | |
| SE24 | | 43-50 | | | |
| SE25 | | 62 | | | |
| SE26 | | 74-80 | | | |
| NPE | 29.9 | | | | |

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Applications Examples AE1 to AE4Example AE1 - Semi Aqueous Cleaners

5 Semi aqueous cleaning involves the cleaning of, e.g. metal,
components with a solvent followed by a water rinse stage. Frequently
solvents derived from terpenes are used in this application. Surface
active agents can be added to expedite the removal of the solvent from
the components being cleaned during the water rinse stage. Such
10 surface active agents, or rinse aids as they are known, must fulfil
two criteria. Firstly they must effect good solvent removal and be
soluble in the cleaning solvent. Secondly they must not stabilise
mixtures of the solvent and water thus preventing effective separation
of the mixture with adverse implications on waste disposal. Materials
15 A and B below have the desired surface active properties to be
effective rinse aids in semi aqueous cleaning formulations. They are
also soluble in terpene solvents. Surprisingly tests have
demonstrated that they exhibit rapid and more effective solvent and
water separation as compared to other surfactants commonly used in
20 this application.

The following experimental data demonstrate the effect.
Mixtures of 0.6% surfactant, 9.4% terpene solvent and 90% water were
prepared by shaking 5 times in a measuring cylinder. The mixtures
were allowed to stand at room temperature for twenty hours, during
25 which time a periodic assessment of the level of phase separation was
made. The following table records the results obtained.

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| | Surfactant | Appearance after 20 Hours | Comments |
|----|---|--|---|
| 5 | None | Both layers clear | Separation complete after 0.5 hours |
| | C10 alcohol 3 EO | Oil and water layers cloudy | Separation incomplete after 20 hours |
| 10 | Alkyl phenol 4.5 EO | Oil and water layers slightly cloudy | Separation complete after 10 hours |
| | SE10 | Oil and water layers very slightly cloudy | Separation complete after 12 hours |
| 15 | SE1 | Slight haze in both layers | Separation complete after 8 hours |
| 20 | Complete separation means oil layer of 10% and a water layer of 90% of the total volume. | | |

Example AE2 - Wool Scouring

Ten 20g samples of wool were washed successfully in the same bath of a 0.1% w/w solution of surfactant in water (1 litre) at 60°C. The residual grease in the last sample to be washed was then measured by extraction with an organic solvent, typically dichloromethane or chloroform. The results are set out in the following table:

| | Product | % Residual Grease |
|----|---|-------------------|
| 30 | "SYNPERONIC" NP9 (**) | 1.71 |
| | "SYNPERONIC" 87K (*) | 2.16 |
| | SE1 | 1.24 |
| 35 | ** Commercially available C ₁₃₋₁₅ alcohol alk xylate | |
| | * Commercially available nonyl phenol ethoxylate | |

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Example AE3 - Wool Scouring

Further tests of wool scouring were carried out using fine merino wool (ca. 20 μm diameter fibres) at a surfactant dose of 0.5 g.l⁻¹ in an aqueous scouring solution containing 4% by weight of KCl (to simulate salt accumulation during repeated use of the scouring solution). The scouring was operated at 65°C in the scour detergent bowls and at 50°C in the rinse bowls. The scouring solutions were reused a number of times and the weight percentage of residual wool wax on the wool after each treatment was noted and is given in Table 3 below. The product of SE1 was compared with four other scouring surfactants:

| Code | Product Name | Source | Description |
|------|----------------|-----------------|------------------------------|
| C3 | Lissapol TN450 | ICI Australia | nonyl phenol ethoxylate |
| C4 | Lissapol BD20 | ICI Australia | biodegradable wool scourer |
| C5 | Lissapol BD30 | ICI Australia | biodegradable wool scourer |
| C6 | Softanol 90 | Nippon Shokubai | secondary alcohol ethoxylate |

Table 3

| Run No | Surfactant | | | | |
|--------|------------|------|------|------|------|
| | SE1 | C3 | C4 | C5 | C6 |
| 1 | 1.13 | 0.81 | 1.08 | 1.02 | 0.77 |
| 2 | 0.96 | 0.95 | 1.38 | 0.87 | 0.73 |
| 3 | 0.96 | 1.22 | 1.15 | 0.89 | 0.86 |
| 4 | 0.93 | 1.02 | 1.10 | 1.01 | 0.94 |
| 5 | 0.98 | 1.19 | 1.74 | 0.90 | 1.04 |
| 6 | 0.93 | 1.07 | 1.36 | 1.12 | 0.97 |
| 7 | 0.98 | 1.02 | 1.18 | 1.02 | 1.19 |
| 8 | 1.04 | 1.20 | 1.76 | 1.17 | 1.46 |

The results given in Table 3 show that the compound of this invention performs well as a wool scouring agent and in particular shows good retention of performance as compared with current agents, even in treating a wool that is known to be difficult to scour.

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Example AE4 - Polyacrylamide Emulsion Inversion

The following mixture was polymerised by heating to about 40°C using as the primary emulsifier a commercially available polymeric surfactant sold under the trade name "HYPERMER" 2296.

| | |
|---|------------|
| Acrylamide | 135.0g |
| Acrylic acid | 58.0g |
| Demin Water | 179.0g |
| Hydrocarbon Solvent (Isopar L) | 168.0g |
| Sodium hydroxide | up to pH 6 |
| Ethylene diamine tetra acetic acid (EDTA) (5%) | 5.2g |
| Azobisisobutyronitrile (AIBN) | 0.4g |
| Primary emulsifier | 8-12g |

3% of each of the surfactants below was added as an inverting agent to a sample of the polymer emulsion and the mixture allowed to rest for 2-3 days. A sample of emulsion was then taken and a 1% blend in water produced. After 2 minutes of stirring the viscosity was measured. Stirring was then continued and after 15 minutes the viscosity was measured again. The measured viscosities were:

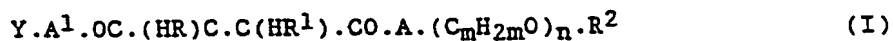
| | Viscosity (mPa.s) | |
|------------------|-------------------|---------------|
| | After 2 mins | After 15 mins |
| "SYNPERONIC" NP9 | 12000 | 26000 |
| SE11 | 11500 | 26000 |
| SE19 | 24000 | 24500 |
| C3 | coagulated | - |

These results show that SE11 is equivalent to the conventional inverting agent "SYNPERONIC" NP9 and SE19 is superior and that compound C3 does not act effectively as an inverting agent.

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Claims

- 1 A compound of the formulae (I) or (II):



where

one of R and R¹ is C₆ to C₂₂ alkenyl or alkyl and the other is hydrogen;

A is - O - or or -NR⁴-, where R⁴ is hydrogen or C₁ to C₆ alkyl;

n is 2 to 100;

m is 2 or 3 (and may vary along the polyoxyalkylene chain);

R² is hydrogen or C₁ to C₆ alkyl;

A¹ is - O -, - O⁻ or -NR⁴-, where R⁴ is hydrogen or C₁ to C₆ alkyl;

such that

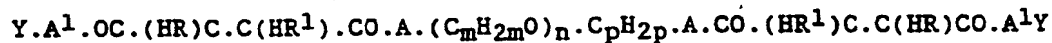
when A¹ is - O⁻, Y is a cation; and

when A¹ is - O - or -NR⁴-:

Y is a C₁ to C₆ alkyl group (R³) or a group of the formula (C_mH_{2m}O)_n.R², where m, n and R² are independently as defined above;

provided that when A is - O - or A¹ is - O⁻ the total number of carbon atoms in the groups R, R¹ and any groups R² and R³ is at least 13.

or



where:

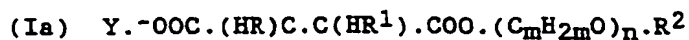
(II)

n, m and each R, R¹, A, A¹ and Y are independently as defined above; and

p is 2 or 3.

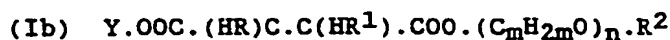
- 2 A compound as claimed in claim 1 in which one of R and R¹ is C₁₄ to C₂₂ alkenyl or alkyl and the other is hydrogen.

- 3 A compound as claimed in claim 1 of the formula (Ia):



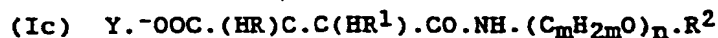
where m, n and R^2 are as defined in claim 1; Y is a cation and one of R and R^1 is a C_{14} to C_{22} alkenyl or alkyl group and the other is hydrogen.

- 4 A compound as claimed in claim 1 of the formula (Ib):



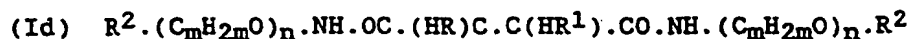
where R, R^1 , m, n and R^2 are as defined in claim 1; and Y is a C_1 to C_6 alkyl group or a group of the formula $(C_mH_{2m}O)_n.R^2$ where m, n and R^2 are independently as defined in claim 1.

- 5 A compound as claimed in claim 1 of the formula (Ic):



where R, R^1 , m, n and R^2 are as defined in claim 1 and Y is a cation.

- 6 A compound as claimed in claim 1 of the formula (Id):



where R and R^1 and each m, n and R^2 is independently as defined in claim 1.

- 7 A compound as claimed in any one of claims 4 to 6 in which one of R and R^1 is a C_{14} to C_{22} alkenyl group and the other is hydrogen.

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- 8 A compound as claimed in any one of claims 1 to 7 wherein
m is 2;
p, if present, is 2;
n is from 3 to 50 and
Y is a cation it is H^+ , an alkali metal cation, or an ammonium cation, or a methyl, ethyl or butyl group.
- 9 A method of treating wool to remove wool wax which method comprises washing the wool, containing wool wax, with an aqueous mix including an effective amount of a compound of the formulae (I) or (II) as defined in any one of claims 1 to 8.
- 10 A method as claimed in claim 9 wherein the compound is a compound of the formula (Ia) where m is 2, n is from 3 to 10 and where R^2 is a C_1 to C_6 alkyl group.
- 11 A method of inverting a water in oil emulsion containing polyacrylamide in the aqueous phase which comprises including in the water in oil emulsion a compound of the formulae (I) or (II) as defined in any one of claims 1 to 8 and subsequently diluting the water in oil emulsion into water to invert it.
- 12 A method as claimed in claim 11 wherein the compound is a compound of the formula (Ia) where m is 2, n is from 8 to 25, and R^2 is H or a C_1 to C_6 alkyl group.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/01335

| | | |
|--|---|---|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08G65/32; D01C3/00; C11B11/00; C08F20/56 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.Cl. 5 | C08G | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ⁹ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
| X | WO,A,8 700 856 (THE LUBRIZOL CORPORATION) 12 February 1987 see claim 1 see page 7, paragraph 2 see page 8, paragraph 1 see page 8, paragraph 2 see page 9, line 6 - line 8 --- | 1,2,7-8 |
| X | GB,A,2 131 820 (CHEVRON RESEARCH CO.) 27 June 1984 see examples 1,2 --- | 1-3,7,8 |
| X | EP,A,0 384 605 (TEXACO DEVELOPMENT CORP.) 29 August 1990 see claim 1 see page 6, line 15 - line 55 --- | 1,2,6,7, 8 |
| -/- | | |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | | Date of Mailing of this International Search Report |
| 24 SEPTEMBER 1993 | | 12.10.93 |
| International Searching Authority | | Signature of Authorized Officer |
| EUROPEAN PATENT OFFICE | | O'SULLIVAN T.P. |

Form PCT/ISA/210 (second sheet) (January 1985)

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
|--|---|-----------------------|
| Category ° | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
| A | EP,A,0 107 199 (CHINOIN ETC) 2 May 1984 cited in the application see claims 1-3 ----- | 1,2,8-12 |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9301335
SA 75532

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on

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24/09/93

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO-A-8700856 | 12-02-87 | US-A- 4661275 | 28-04-87 |
| | | AU-B- 595226 | 29-03-90 |
| | | AU-A- 6144186 | 05-03-87 |
| | | EP-A,B 0231287 | 12-08-87 |
| | | JP-T- 63500725 | 17-03-88 |
| | | US-A- 4749500 | 07-06-88 |
| GB-A-2131820 | 27-06-84 | BE-A- 898441 | 30-03-84 |
| | | DE-A- 3345058 | 14-06-84 |
| | | DE-A- 3348402 | 19-03-92 |
| | | FR-A- 2537454 | 15-06-84 |
| | | JP-A- 59115733 | 04-07-84 |
| | | NL-A- 8304253 | 02-07-84 |
| | | SE-B- 459789 | 07-08-89 |
| | | SE-A- 8306812 | 14-06-84 |
| | | US-A- 4695401 | 22-09-87 |
| | | US-A- 4915786 | 10-04-90 |
| EP-A-0384605 | 29-08-90 | US-A- 4968321 | 06-11-90 |
| | | AU-B- 621710 | 19-03-92 |
| | | AU-A- 4913890 | 09-08-90 |
| | | CA-A- 2009287 | 06-08-90 |
| EP-A-0107199 | 02-05-84 | EP-A,B 0032289 | 22-07-81 |

EPO FORM P0019

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82